Ball-milled Si powder for the production of H_2 from water for fuel cell applications

Lang Xu [a], Sobia Ashraf [a], Jingping Hu [a], Peter P. Edwards [b], Martin O. Jones [c], Emina Hadzifejzovic [a], John S. Foord [a,]*

[a] *Chemistry Research Laboratory, Department of Chemistry, University of Oxford, Mansfield Road, Oxford, OX1 3TA, United Kingdom*

[b] *Inorganic Chemistry Laboratory, Department of Chemistry, University of Oxford, South Parks Road, Oxford, OX1 3QR, United Kingdom*

[c] *Science and Technology Facilities Council, Rutherford Appleton Laboratory, Harwell Campus, Didcot, OX11 0QX, United Kingdom*

* Corresponding author. Tel: +44 01865 275967. Email: john.foord@chem.ox.ac.uk

Abstract

The development of a safe technique for the supply of hydrogen to small portable fuel cells has emerged as a significant barrier to their deployment in recent years, with solutions centering on the use of hydrogen absorption materials, or the generation of hydrogen through chemical reaction. In the present work we demonstrate that the ball-milling of Si under inert conditions in the presence of KOH and sucrose results in the formation of a fine Si-based powder which reacts spontaneously with water at ambient starting temperature to evolve hydrogen rapidly at high yield. Embedded KOH is capable of accelerating the hydrolysis reaction of silicon by the self-heating effect attributed to dissolution heat of KOH, obviating the need for external heating to initiate the reaction; it also reduces the sensitivity of the reaction to oxide contamination of the Si surface by enabling its dissolution in the form of soluble silicates. Moreover, the silicon-water reaction can be switched on and off by adjusting the ambient temperature. It is shown that ball-milled, KOH-embedded Si powder is able to react with different water sources, such as tap water, river water, and salt water, to produce H_2 under aerobic conditions. The method represents a cheap scalable approach for the safe provision of hydrogen fuel to small fuel cells.

Keywords: hydrogen fuel cell; silicon; silicon-water reaction; ball milling

1. Introduction

As an energy carrier, H_2 is one of the best fuels for mobile fuel cell applications, such as domestic appliances and automobiles, due to its high-energy density by weight and the absence of undesirable reaction products [1-5]. However, the efficient H_2 supply to small portable fuel cells remains challenging because the liquefaction of hydrogen only occurs below the extremely low temperature (20.3 K), which requires expensive cryogenic systems and high-energy consumption [6]. High-pressure hydrogen tanks have been used in some concept fuel cell cars, but compressed hydrogen at high pressure represents a potential danger, and it is especially difficult to implement safely in small mobile fuel cell applications where strong engineered structures are not present [7]. Thus it is attractive to develop safe alternative methods for on-demand supply of H_2 which avoids the use of high pressures. One approach is the use of hydrogen storage compounds which absorb hydrogen reversibly and release it again when heated, but these materials have had limited success due to difficulties in reversibly cycling the materials and tuning the materials to absorb and desorb hydrogen to obtain required yields in convenient temperature and pressure regimes [6].

A variety of convenient chemical reactions to generate hydrogen on demand have therefore been examined including H_2 production by hydrolysis reactions of aluminium and its alloys [8-16]. In terms of this latter approach, which is of particular interest in this paper, it can be noted that silicon has advantages over aluminium in terms of H_2 production: *(1)* On a mass basis, one gram of Si can produce 0.14 gram of H_2, while the same mass of Al can generate 0.11 gram of H_2, thus showing higher energy density of silicon; *(2)* Si makes up about 27% mass of Earth's crust, the second most abundant element next to oxygen and is available at a much lower economic cost than Al [17,18]. Despite this, there have been few reports on the use of silicon in this type of application to date.

The reaction of silicon with water is shown as:

$$\mathrm{Si\ (s) + 2H_2O\ (l) \rightarrow SiO_2\ (s) + 2H_2\ (g)} \qquad (1)$$

This reaction is highly exothermic with a standard enthalpy of reaction of -409 kJ mol^{-1} (298 K) [19]. To be practically useful as a source of hydrogen for fuel cell applications, it is highly advantageous that the reaction can start off at room temperature to avoid the use of an external power supply to provide auxiliary heating and that a high reaction yield can be obtained. Although the irreversibility and exothermicity of the reaction indicate the reaction might satisfy these criteria, Si scarcely reacts with water under ambient conditions because a passivation layer of silica forms at the silica-water interface which blocks the reaction. To solve this problem, highly alkaline water has been used to remove the oxide layer [20-23] and sophisticated methods such as laser pyrolysis [20] have been used to prepare unpassivated Si in nanoparticle form to maximize the surface area available for reaction. However, despite the progress, a simplified, practically useful route to hydrogen production by the utilization of silicon has not been demonstrated.

In the present work such a procedure is shown for the first time – a scalable process involving ball-milling granulated Si in the presence of KOH and sucrose yields a powder which spontaneously reacts with water at room temperature to produce H_2 rapidly with a relatively high yield. KOH becomes embedded in the

Si powder by the ball-milling process, rather than directly dissolved in water, so that *(1)* the heat of dissolution of KOH can be utilized to accelerate the hydrolysis of silicon and *(2)* the dissolution of KOH and sucrose helps disperse the Si powder in the water medium and the KOH also serves to dissolve any oxide formed on the Si surface in the form of soluble silicates. Reacted with distilled water at room temperature (~20 °C), the ball-milled Si powder embedded with KOH and sucrose is able to achieve 75% yield in an inert atmosphere and 71% yield under an aerobic condition, demonstrating its O_2-tolerant capacity for H_2 production. Such KOH-embedded Si powder can also react with non-pure water, including tap water, river water, and salt water, expanding sources of water that can be used to produce H_2.

2. Experimental

2.1. Materials

Silicon lumps (≥98.5%), potassium hydroxide (≥90%), sucrose (≥99.5%), anhydrous acetonitrile (≥99.8%), and sodium chloride (≥99%) were purchased from Sigma-Aldrich and used without further purification. The silicon lumps were crushed to small pieces by a hydraulic press under a pressure of 5 tonnes. Distilled water was obtained from a Milli-Q water system (18 MΩ cm), tap water from laboratory running water, and river water from the River Thames (beside Port Meadow, Oxford); salt water was made by dissolving 3.5 g sodium chloride in 100 mL distilled water.

2.2. Preparation of ball-milled Si powder

Si lumps, KOH, and sucrose were wet milled in a Fritsch Pulverisette 7 milling machine. To avoid excess heating the milling programme was: milling for 10 min at 900 rpm → pausing for 10 min → milling for 10 min at 900 rpm. In a typical preparation, 0.7 g Si lumps, 0.2 g KOH, 0.1 g sucrose, and 3 mL anhydrous acetonitrile were added in a milling cup containing 50 tempered-steel balls (diameter: 5 mm) in a glove box (MTI corporation). The milling cups were tightly sealed to prevent the oxidation of silicon during the milling process. Ball-milled Si powder was then dried by the evaporation of acetonitrile in the glove box and ready to use. To prepare ball-milled Si powder containing Si only, Si with 10% sucrose, and Si with 20% KOH, 1 g Si lumps, 0.9 g Si lumps with 0.1 g sucrose, and 0.8 g Si lumps with 0.2 g KOH were mixed with 3 mL anhydrous acetonitrile in the milling cup containing 50 tempered-steel balls, respectively. For the preparation of ball-milled Si powder containing 10%, 30%, and 40% KOH, 0.8 g Si lumps + 0.1 g KOH + 0.1 g sucrose, 0.6 g Si lumps + 0.3 g KOH + 0.1 g sucrose, 0.5 g Si lumps + 0.4 g KOH + 0.1 g sucrose were mixed with 3 mL anhydrous acetonitrile in the milling cup containing 50 tempered-steel balls, respectively. The ball-milled powder was stored in the glove box under nitrogen until used.

2.3. H_2 production by the hydrolysis reaction of Si powder

A quantity (0.16 g) of the ball-milled Si powder was added to a specimen tube with a Suba Seal stopper, through which a needle for gas outlet and a thermocouple wire passed. For anaerobic experiments, water was purged of O_2 by bubbling N_2 for 2 hours and a certain amount (*e.g.* 0.5 mL, 1 mL, 2 mL, or 4 mL) of the purged water was subsequently injected into the Si powder, followed by gently shaking the tube to allow for the thorough mix of the reactants. For aerobic experiments, a certain type of water (*e.g.* distilled water, tap water, river water, or salt water) was directly used without being purged and the typical procedure was: opening the stopper and adding the non-purged water to the Si powder under air → shaking the specimen tube for 30 seconds to make the reaction system fully exposed to air → closing the stopper for H_2 collection. Adjusting the ambient temperature was achieved by immersing the specimen tube in a water bath at a certain temperature (*e.g.* 50 °C or 90 °C) or an ice-water bath (0 °C). An inverted graduated cylinder in a water basin was used to collect and measure the produced H_2. The thermocouple that was connected to a computer provided temperature data of the internal reaction system. X-ray diffraction (XRD) patterns of the reacted powder as well as un-milled Si lumps and un-reacted ball-milled Si powder were recorded on a PANAnalytical X'pert diffractometer equipped with a Cu Kα radiation source ($\lambda = 1.54178$ Å). Scanning electron microscopy (SEM) image was recorded on a Hitachi 520 operating at an accelerating voltage of 20 kV.

3. Results and discussion

3.1. The silicon-water reaction

Si powder was prepared as described above and its characteristics for reaction with water examined. Fig. 1A shows typical results for the volume of produced H_2 and the temperature change of the reaction of ball-milled Si powder containing 70% Si, 20% KOH, and 10% sucrose with distilled water without stirring under the anaerobic atmosphere at the initial ambient temperature of 19 °C. The H_2-production rate underwent a quick-slow-quick-slow variation in evolution rate while the temperature showed a two-peak configuration, indicating that there was a positive correlation between the production rate and the reaction temperature. The reaction process could be divided into four stages according to temperature change: *(1) 0~5 min* – the rate was 45 mL g^{-1} min^{-1} and the temperature sharply increased from 19.2 °C to 29.5 °C; *(2) 5~20 min* – the reaction rate declined to 10 mL g^{-1} min^{-1} and the temperature decreased to 25.8 °C; *(3) 20~40 min* – the reaction rate rebounded to 23 mL g^{-1} min^{-1} while the temperature reached its maximum 31.5 °C; *(4) beyond 40 min* – the rate and temperature slowed down and the total volume of generated H_2 was 1277 mL g^{-1} with the yield of 75% after three hours. Very little temperature change or hydrogen production was generally observed if KOH is omitted from the reaction mixture and the initial temperature rise correlates quite well with how much KOH is added to the Si product. The most likely observation for this behaviour is that the spontaneous temperature rise in the internal reaction system is attributed to the dissolution of KOH in water which provides sufficient local heating to start the hydrolysis reaction of silicon resulting in hydrogen production. This latter process is itself exothermic resulting in the second peak in temperature and the more extensive evolution of hydrogen.

Fig. 1B shows XRD patterns of the as-received Si lumps, the ball-milled Si powder, and the reacted powder after hydrolysis. All the diffraction peaks of the Si lump and the ball-milled Si powder could be assigned to the cubic phase of silicon [24]. No silicate diffraction peaks were found in the reacted powder, indicating the formation of amorphous silicates, whereas two weak diffraction peaks (*i.e.* 111 and 220) of silicon could be observed, showing there remained un-reacted Si residues. Fig. 1C shows the SEM image of the ball-milled Si powder, with the average size of 2 μm.

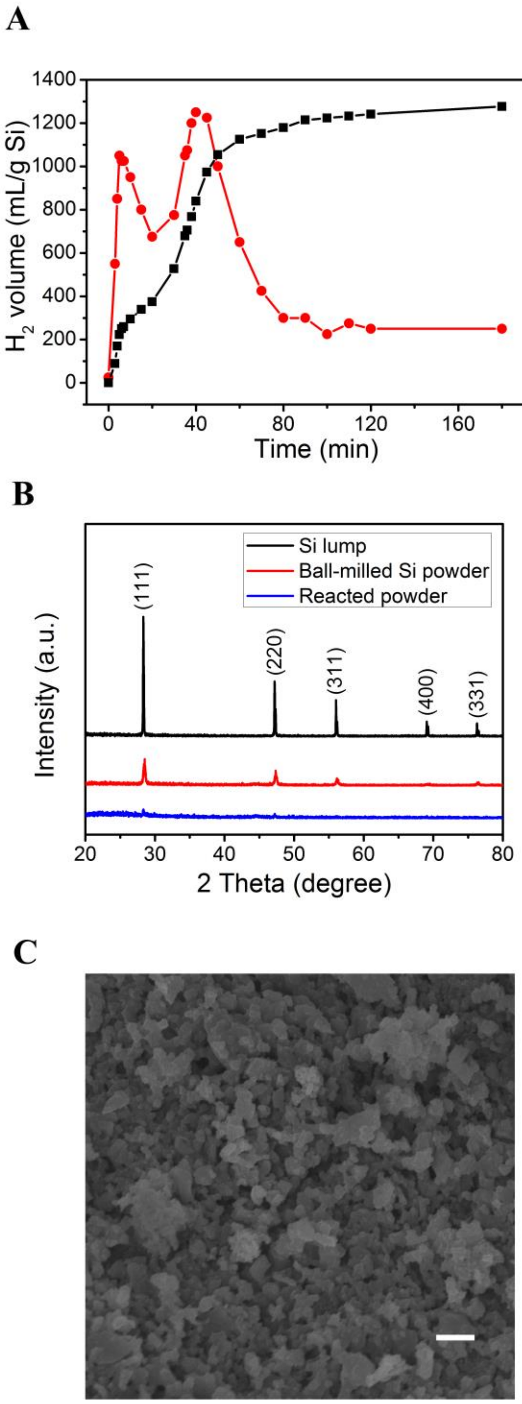

Fig. 1. (A) Dependences of volume of produced H_2 (black) and temperature change (red) on time of the reaction of 0.16 g ball-milled Si powder containing 70% Si, 20% KOH, and 10% sucrose with 2 mL distilled water without stirring in the inert atmosphere at the ambient temperature of 19 °C. (B) XRD patterns of the Si lump (black), the ball-milled Si powder (red), and the reacted powder after hydrolysis (blue). (C) SEM image of the ball-milled Si powder (scale bar represents 5 μm).

3.2. The role of KOH and sucrose as co-milling agents

KOH and sucrose were embedded in the Si powder during the milling process when present in the milling mixture. To study the effect of KOH and sucrose on the H_2-production activity of ball-milled Si powder, three different kinds of Si powder were prepared by milling Si lump only, Si lump with sucrose (10%), and Si lump with KOH (20%), respectively. The three kinds of ball-milled Si powder were reacted with water without stirring under the anaerobic condition, as shown in Fig. 2. The Si powder without KOH or sucrose showed negligible activity of H_2 production with the volume of produced H_2 was only 50 mL g^{-1} (yield: 3%) over three hours. The Si powder containing only sucrose also had a low activity of H_2 production (volume: 140 mL g^{-1} and yield: 8%), while the H_2-production activity of Si powder containing only KOH increased substantially (volume: 984 mL g^{-1} and yield: 57%) though it is still lower than that of Si powder containing both KOH and sucrose noted in Fig. 1A (volume: 1277 mL g^{-1} and yield: 75%). The role of KOH makes the reaction with water much less sensitive to the presence of surface oxide by providing a source of heat from dissolution to accelerate the reaction and by converting SiO_2 to soluble silicates [25], thus exposing internal un-reacted silicon to water:

$$2SiO_2\ (s) + 2OH^-\ (aq) \rightarrow Si_2O_5^{2-}\ (aq) + H_2O\ (l) \qquad (2)$$

The presence of sucrose makes the powder disperse much better in the water, by itself dissolving to create a porous structure to enable water to penetrate the powder. Therefore, co-milling both KOH and sucrose with the Si is able to make an improved interaction with the water thus increasing the H_2-production yield, as shown in Fig. 3.

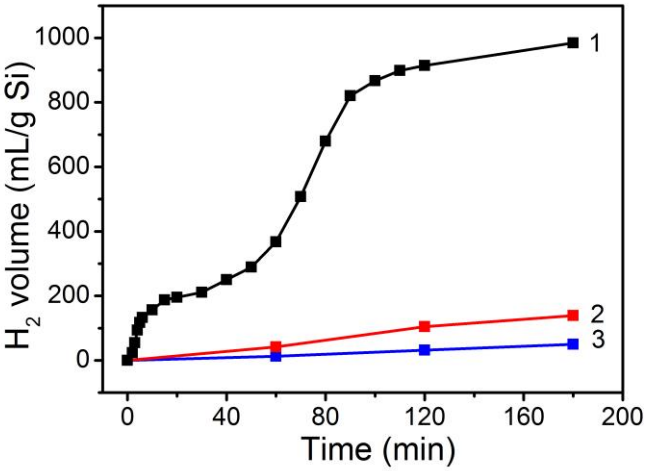

Fig. 2. Dependences of volume of produced H_2 on time of the reactions of 0.16 g ball-milled Si powder containing (1) 80% Si + 20% KOH (black), (2) 90% Si + 10% sucrose (red), and (3) 100% Si (blue) with 2 mL distilled water.

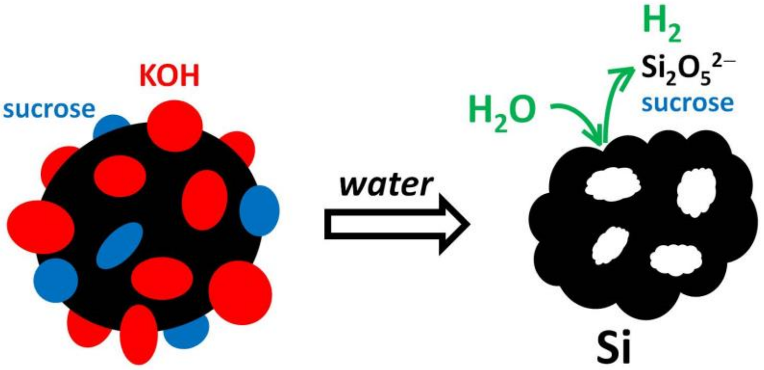

Fig. 3. Schematic representation of how KOH and sucrose-embedded Si powder produces H_2 by the reaction with water.

3.3. Effect of KOH concentration

The concentration of KOH in the ball-milled Si powder has considerable influence over its activity of H_2 production. The reactivity of Si powder containing different concentrations of KOH with distilled water without stirring under the anaerobic atmosphere is shown in Fig. 4. In the initial five minutes, the H_2-production rates of Si powder containing 30% and 40% of KOH were 81 mL g^{-1} min^{-1} and 138 mL g^{-1}

min^{-1}, respectively, much higher than the rate of Si powder containing 20% KOH (45 mL g^{-1} min^{-1}) at the same stage. Heat released by high concentrations of KOH heated the reaction system quickly and the rapid increase in temperature during a short period of time massively increased the reaction rate. However, the H_2 yields produced by the Si powder containing 30% KOH and 40% KOH were 70% and 60% over three hours, respectively, both of which were lower than that by the Si powder containing 20% KOH (75%). Owing to its high affinity with water, excessive KOH could 'desiccate' the reaction system so that silicon became not readily accessible to enough amount of water, thereby leading to the decrease in yield. The effect of water amount on the H_2-production activity will be discussed below. For the Si powder containing 10% KOH, less dissolution heat due to lower concentration of KOH could not significantly increase the temperature of reaction system so that the H_2-production rate was very low until it gradually increased to 2~4 mL g^{-1} min^{-1} after 80 minutes, and the volume of produced H_2 was only 391 mL g^{-1} (yield: 23%) after three hours. Therefore, it is important to balance the amount of KOH, not only capable of accelerating the hydrolysis reaction rate but also allowing for availability of sufficient water for silicon.

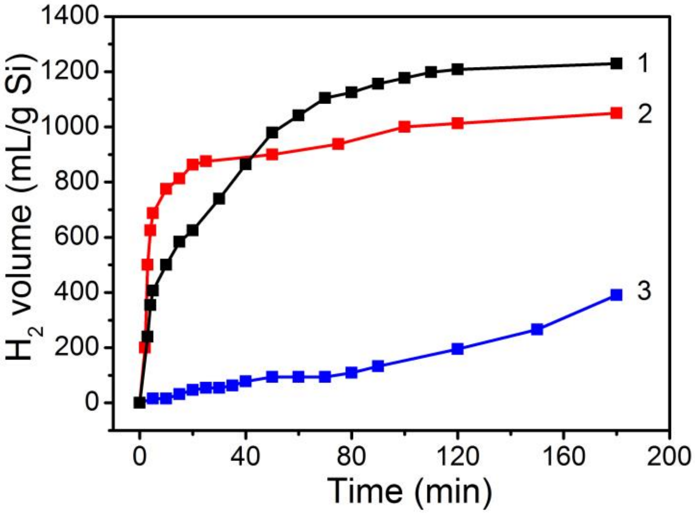

Fig. 4. Dependences of volume of produced H_2 on time of the reactions of 0.16 g ball-milled Si powder containing (1) 60% Si + 30% KOH + 10% sucrose (black), (2) 50% Si + 40% KOH + 10% sucrose (red), and (3) 80% Si + 10% KOH + 10% sucrose (blue) with 2 mL distilled water.

3.4. Effect of water addition

Stoichiometrically, 0.16 g of the ball-milled Si powder containing 70% Si, 20% KOH, and 10% sucrose requires only 0.15 mL water (Eq. 1). However, owing to the high affinity of KOH for water and the need for the dispersal of Si powder, much larger quantity of water than the theoretical amount is required. On the other hand, excessive water would mitigate the self-heating effect of KOH due to the large heat capacity of water. To study the effect of water amount on the H_2-production activity of the ball-milled Si powder, 0.16 g of the Si powder containing 70% Si, 20% KOH, and 10% sucrose was reacted with 0.5 mL, 1 mL, and 4 mL distilled water without stirring under the anaerobic condition, respectively, as shown in Fig. 5 (for 2 mL, see Fig. 1A). As expected, the H_2-production rate in the initial five minutes was in inverse proportion to the volume of added water: 0.5 mL (71 mL g^{-1} min^{-1}) > 1 mL (61 mL g^{-1} min^{-1}) > 2 mL (45 mL g^{-1} min^{-1}) > 4 mL (7 mL g^{-1} min^{-1}). After three hours, the order of the total volume of produced H_2 was: 2 mL (1277 mL g^{-1}, yield: 75%) > 1 mL (1232 mL g^{-1}, yield: 72%) > 4 mL (1143 mL g^{-1}, yield: 67%) > 0.5 mL (1045 mL g^{-1}, yield: 61%). The H_2-volume curves for 4 mL and 0.5 mL water intersected at 40 min and the volume of H_2 produced in the 4 mL water exceeded that in the 0.5 mL water after this point. Though surplus water (4 mL) would mitigate the self-heating effect of KOH and lower the reaction rate in the initial stage, it was easily accessible to silicon; as to insufficient water (0.5 mL), water was persistently consumed as the reaction proceeded, making the water shortage more severe and thus limiting the extent of reaction. As mentioned above, insufficient amount of usable water due to excessive KOH (*e.g.* the Si powder containing 40% KOH) had the similar effect on the H_2-production yield.

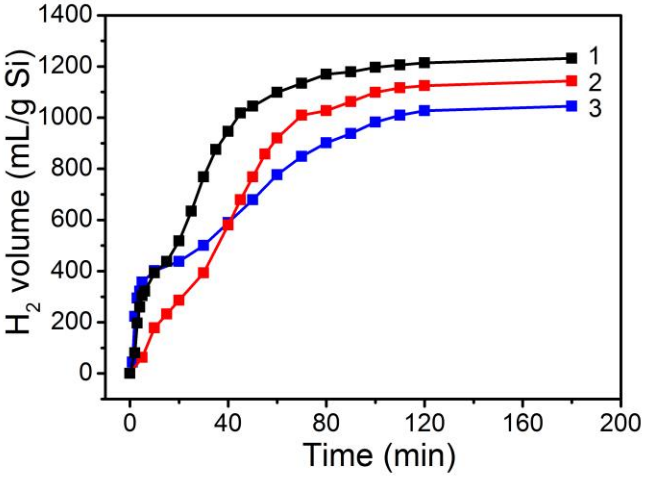

Fig. 5. Dependences of volume of produced H_2 on time of the reactions of 0.16 g ball-milled Si powder containing 70% Si, 20% KOH, and 10% sucrose with (1) 1 mL (black), (2) 4 mL (red), and (3) 0.5 mL (blue) distilled water. Common conditions: without stirring, inert atmosphere, and ambient temperature: 19 °C.

3.5 Influence of ambient temperature

The dissolution and reaction heat from the internal reaction system is able to change the H_2-production rate and yield. Likewise, adjusting the ambient temperature can also alter the rate and extent of the hydrolysis reaction of silicon so as to control on/off of H_2 production. Fig. 6A shows the H_2-volume curves for the reaction of Si powder containing 70% Si, 20% KOH, and 10% sucrose with distilled water without stirring at the ambient temperatures of 90 °C, 50 °C, and 0 °C under the anaerobic condition. At 90 °C, the H_2-production rate was 714 mL g^{-1} min^{-1} and the volume of produced H_2 was 1071 mL g^{-1} (yield: 62%) in just 1.5 min, and the volume further increased to 1286 mL g^{-1} (yield: 75%) in 3 min. As the total volume of produced H_2 was 1428 mL g^{-1} (yield: 83%), 90% completion of this reaction required only three minutes. At 50 °C, the H_2-production rate was 193 mL g^{-1} min^{-1} and the yield was 56% in the initial 5 min, while the total H_2 yield after the 3-hour reaction was 77%, showing that five minutes reached 72% completion of the reaction. Thus raising the ambient temperature above 50 °C satisfies a rapid supply of H_2. At the other extreme, the yield of the hydrolysis reaction for three hours at the ambient temperature of 0 °C was 11%, indicating that such a low temperature could slow down and even stop the reaction. Therefore, it is possible to control the switch of the H_2-production reaction by regulating the ambient temperature (*on* at 20 °C and *off* at 0 °C). Fig. 6B shows how the hydrolysis reaction of the ball-milled Si powder containing 70% Si, 20% KOH, and 10% sucrose was controlled by ambient temperature. In the initial 30 min, the reaction proceeded at the ambient temperature of 20 °C; compared to Fig. 1A in the same period (0~30 min), the two curves were identical in the volume of produced H_2 and the reaction rate. The ambient temperature was then lowered to 0 °C and kept for ten minutes; no H_2 was produced in this period, during which time the same reaction system could generate 313 mL g^{-1} of H_2 if the ambient temperature remained 20 °C (Fig. 1A). After the ambient temperature rose again to 20 °C at 40 min, the reaction rate recovered, showing that the switch of hydrolysis reaction by adjusting ambient temperature was reversible. The volume of generated H_2 at 195 min was 1196 mL g^{-1}, less than the volume (1277 mL g^{-1}) obtained in the same reaction without the 10-min 'off' (Fig. 1A). To accelerate the reaction, the ambient temperature was increased to 50 °C at 195 min and additional 150 mL g^{-1} of H_2 was produced in ten minutes. Since the Si powder and water formed inseparable slurry, adjusting the ambient temperature is a feasible method for the H_2-production switch.

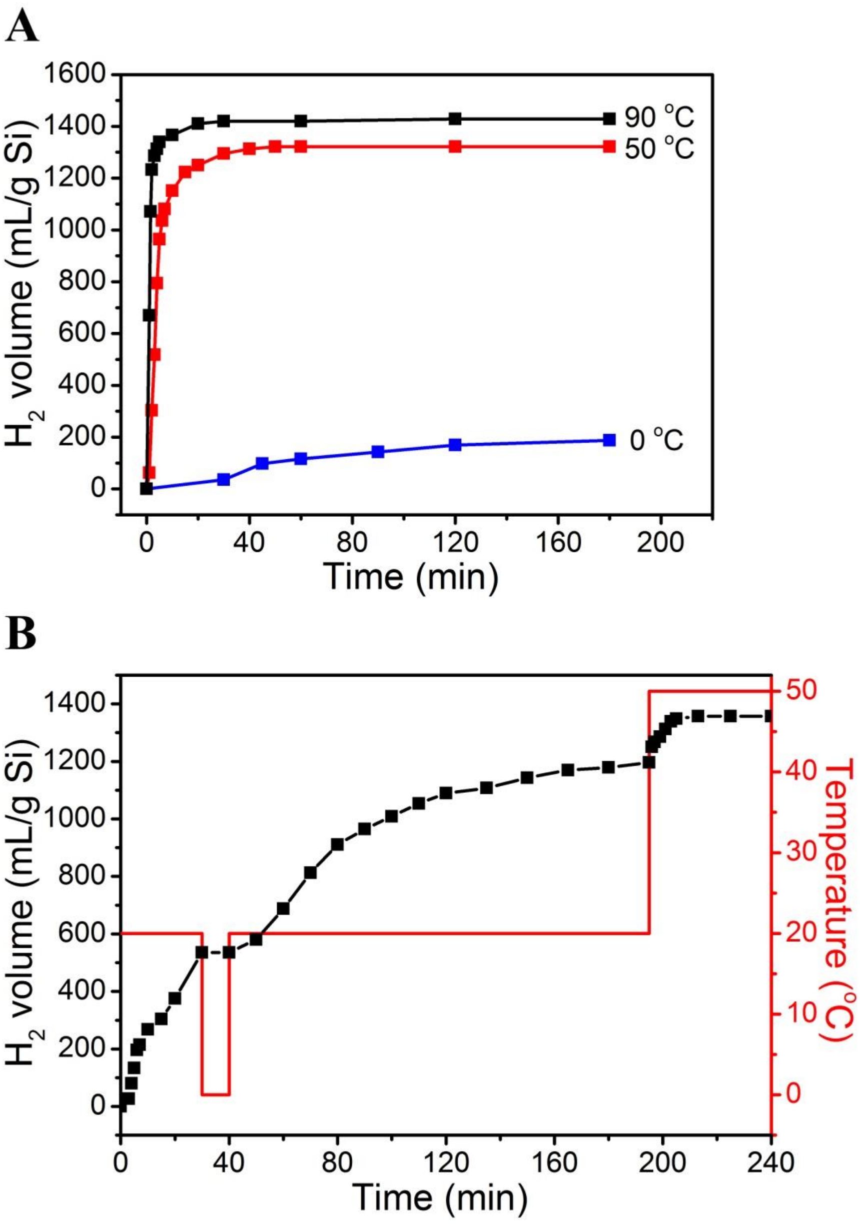

Fig. 6. (A) Dependences of volume of produced H_2 on time of the reactions of 0.16 g ball-milled Si powder containing 70% Si, 20% KOH, and 10% sucrose with 2 mL distilled water without stirring in the inert atmosphere at the ambient temperature of 90 °C (black), 50 °C (red), and 0 °C (blue). (B) Dependence of volume of produced H_2 on time (black) of the reactions of 0.16 g ball-milled Si powder containing 70% Si, 20% KOH, and 10% sucrose with 2 mL distilled water without stirring in the inert atmosphere at the varied ambient temperature (20 °C, 30 min → 0 °C, 10 min → 20 °C, 155 min → 50 °C, 45 min), as indicated in red.

3.6. H_2 production under air from various water sources

The results described above relate to H_2 production under nitrogen ambience to minimize the superficial oxidation which inhibits the reaction. From the simplicity of fabrication, however, it would be preferable to avoid this requirement. Fig. 7A shows the H_2-volume and temperature change of the reaction of ball-milled Si powder containing 70% Si, 20% KOH, and 10% sucrose with distilled water without stirring under air at the ambient temperature of 19 °C. The volume and temperature curves under the aerobic condition were similar to those under the anaerobic condition (Fig. 1A). The hydrolysis reaction can be also segregated into the same four stages: *(1) 0~5 min* – the H_2-production rate was 48 mL g^{-1} min^{-1} and the temperature dramatically increased from 19 °C to 35.8 °C (maximum); *(2) 5~20 min* – the rate decreased to 12.5 mL g^{-1} min^{-1} and the temperature fell to 28.8 °C; *(3) 20~40 min* – the rate rose to 22 mL g^{-1} min^{-1} and the temperature increased to 31.2 °C; *(4) beyond 40 min* – the rate and temperature went down and the overall yield achieved 71% after three hours compared with the yield of 75% under the anaerobic condition. There is very little discrepancy in the H_2-production rates and yields between the aerobic and anaerobic conditions, whereas the major difference lies in the temperature curves. Though both of the temperature curves showed two-hump configurations and the temperature at the second peaks was of the same value, the maximum temperature under the aerobic condition was achieved at the first peak while the maximum temperature under the anaerobic condition was obtained at the second peak, and the former (35.8 °C) was even higher than the latter (31.5 °C). This is because the reaction of Si with O_2 occurred:

$$\mathrm{Si\ (s) + O_2\ (g) \rightarrow SiO_2\ (s)} \qquad (3)$$

The standard enthalpy of this reaction is –904 kJ mol^{-1} (298 K) [19], much larger than that of the hydrolysis reaction of silicon, thus the reaction system rapidly reached the maximum temperature. KOH etched SiO_2 formed by the Si oxidation so that the hydrolysis reaction of Si powder could further proceed. As the reaction went on, steadily produced H_2 purged water surrounding silicon particles of air, so reaction sites on the Si powder became not completely exposed to air, leading to the quite similar H_2-volume curves under the aerobic and anaerobic conditions. Therefore, KOH is the key to O_2 tolerance of the Si powder. The slightly inferior yield under the aerobic condition was attributed to the oxidation of a small amount of silicon.

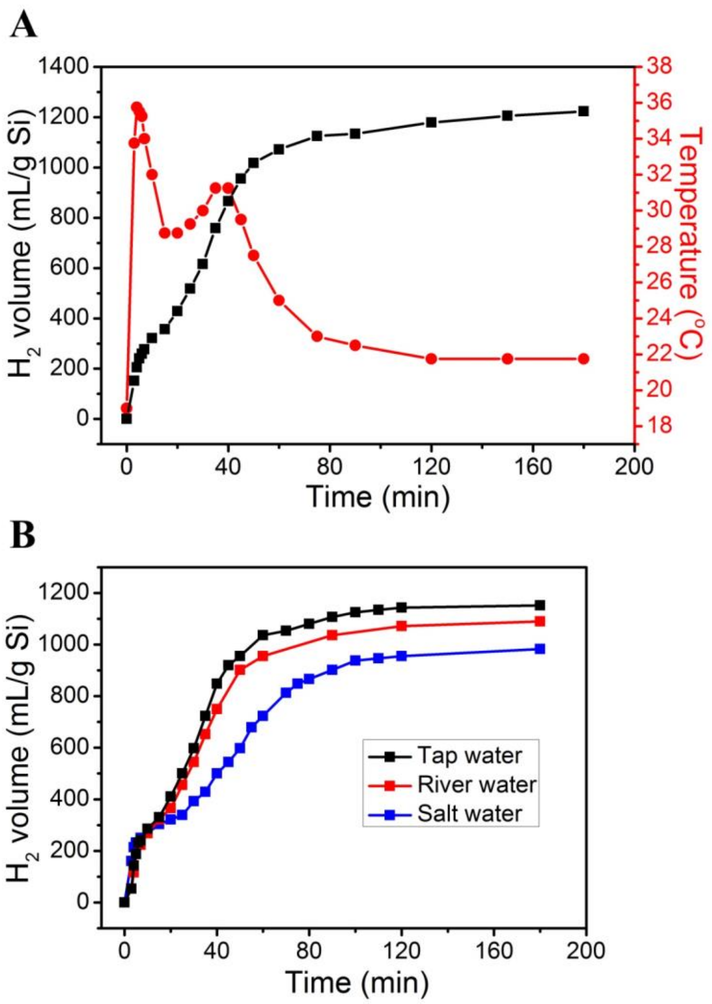

Fig. 7. (A) Dependences of volume of produced H_2 on time (black) and temperature change (red) of the reaction of 0.16 g ball-milled Si powder containing 70% Si, 20% KOH, and 10% sucrose with 2 mL distilled water without stirring under the aerobic condition at the ambient temperature of 19 °C. (B) Dependences of volume of produced H_2 on time of the reactions of 0.16 g ball-milled Si powder containing 70% Si, 20% KOH, and 10% sucrose with 2 mL (1) tap water (black), (2) river water (red), and (3) salt water (blue) without stirring under the aerobic condition at the ambient temperature of 19 °C.

In practical applications, H_2 ought to be produced from various water sources, especially natural water (*e.g.* river water and seawater), other than distilled water only. Tap water, river water from the

Thames, and salt water containing 3.5% NaCl (artificial seawater) were used to react with the ball-milled Si powder containing 70% Si, 20% KOH, and 10% sucrose without stirring under the aerobic condition at the ambient temperature of 19 °C, as shown in Fig. 7B. The volumes of H_2 produced from the three sources at the initial stage were the same while the divergence appeared beyond 10 min. The volume of H_2 produced from tap water, river water, and salt water were 1152 mL g^{-1} (yield: 67%), 1089 mL g^{-1} (yield: 64%), and 982 mL g^{-1} (yield: 57%), respectively, showing that the Si powder was adaptable to a wide range of water conditions (*e.g.* impure and saline).

4. Conclusions

These studies have shown that the H_2-production reaction by ball-milled Si powder embedded with KOH and sucrose can occur at reasonable rates under less strict conditions, including aerobic atmosphere without being purged of air in advance, diverse sources of water including natural water and salt water, room temperature without external heating, and quiescent conditions without stirring or rotating. KOH plays a pivotal role in such advantages: KOH is able to remove the passivation layer (SiO_2) formed on the surface of Si powder, thus allowing the hydrolysis reaction to move forward; this attribute also makes the reaction O_2-tolerant. Either excessive or deficient KOH lowers the volume and yield of produced H_2 ascribed to poor water availability or low internal temperature, thus KOH concentration, water amount, and internal temperature are closely-related factors in the H_2-production performance of Si powder. Adjusting ambient (external) temperature acts as an on-off switch or a fast-forward/pause key of H_2 production, which can therefore be used as a local 'on-demand' H_2 generator for use in conjunction with portable fuel cells.

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Graphical abstract